PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5:
A21D 13/08

A1

(11) International Publication Number: WO 94/00996

(43) International Publication Date: 20 January 1994 (20.01.94)

(21) International Application Number: PCT/EP93/01704
(22) International Filing Date: 30 June 1993 (30.06.93)

(71) Applicant (for all designated States except AU BB CA GB IE

LK MN MW NZ SD): UNILEVER N.V. [NL/NL]; Wee
na 455, NL-3013 AL Rotterdam (NL).

(30) Priority data:

92202112.6 10 July 1992 (10.07.92) EP
(34) Countries for which the regional
or international application
was filed:
93200088.8 14 January 1993 (14.01.93) EP
(34) Countries for which the regional
or international application
was filed:
NL et al.

(71) Applicant (for AU BB CA GB IE LK MN MW NZ SD only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4 4BQ (GB). (72) Inventors: BROCKHUS, Jeroen, Johannes, J., J.; Neubourgstraat 14, NL-4834 JM Breda (NL). LAMMERS, Jannes, Gerrit; Hohenkamp 1, D-2875 Ganderkesee 2 (DE). MOREE, Jeanette, Digna; Mondlanestraat 10, NL-2807 RJ Gouda (NL). RODENBURG, Tileman;

(74) Agent: HARTONG, Richard, Leroy; Unilever N.V., Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL).

Abeltasmanlaan 218, NL-3133 AD Vlaardingen (NL).

(81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

With international search report.

(54) Title: GLAZING AGENT

(57) Abstract

The invention concerns ready-to-use glazing agents with the composition: 1-25 wt.% of liquid oil; 5-15 wt.% of casein or its salts; 0.05-10 wt.% of emulsifier; 0.1-8.0 wt.% of a compound giving a browning, preferably by a Maillard-type of reaction; balance: water. The composition is sterilizable and has a shelf-life after sterilization of more than 3 months.

WO 94/00996 PCT/EP93/01704

GLAZING AGENT

The invention is concerned with glazing agents that are ready to use.

Glazing agents that are not ready to use are known from, e.g., EP 205,195. According to this reference, a glazing agent can be provided comprising a homogenized emulsion of a protein, an edible oil, water and a thin-boiling starch. The thin-boiling starch is applied in order to regulate the viscosity of the emulsion.

10

5

However, the keepability of such a glazing agent was not sufficient. Although this keepability could be increased by drying the glazing agent, the resulting product was no longer ready to use.

15

Therefore, we have performed a study in order to find a glazing agent that:

- is ready to use;
- has the required spreadability, i.e. viscosity;
- 20 shows good keepability.

As a result of this study, we have found that ready-to-use glazing agents fulfilling the above-mentioned requirements have the following composition:

25

35

They are fat-in-water emulsions comprising:

1-25 wt.%, preferably 5-15 wt.%, of a liquid vegetable oil;

5-15 wt.%, preferably 8-11 wt.%, of casein or one of its salts;

0.005-10 wt.% of an emulsifier, preferably 0.01-1.0 wt.% of an emulsifier, in particular one selected from the group of fatty acid monoglycerides and diglycerides from C_{14} - C_{22} , preferably saturated and/or unsaturated C_{16} - C_{18} fatty acids;

0.1-8.0 wt.% of a composition giving a browning upon heating, preferably a Maillard-type reaction, such as lactose, or a milk product containing lactose, amounts of 0.3-3 wt.% being preferred, while suitable milk products are skimmed milk powder or buttermilk powder;

balance : water

5

10

25

30

35

The liquid vegetable oil being defined as an oil being liquid up to 30°C (so: $N_{30} \approx 0$). So, our composition is free of starch or modified starch.

The viscosity of the composition at 20°C is 1-10⁵ mPa.s, preferably 20-200 mPa.s.

The keepability of these compositions is very satisfactory as the compositions can be sterilized by UHT treatment, i.e. 1-30 seconds at 130-160°C. After this treatment, the viscosity of the glazing agent remains within the specifications, while keepabilities (ambient shelf-lives) are obtained for at least 3 months.

The best results are obtained by applying a liquid vegetable oil with a solid fat index at 20°C of less than 7.0, a preferred oil being a medium-hardened soybean oil.

This liquid oil can also comprise some amount, in particular 2-15 wt% on oil, of a hydrogenated vegetable fat. A preferred fat being hydrogenated palm oil, in particular PO-45. Application hereof improves the viscosity and the stability of the product.

It was further found, that the desired colouring, due to heating of a food product provided with a layer of our glazing agents, could be obtained, when our compositions contained 0.1-8.0 wt% of a compound or a mixture that can give a a browning upon heating, preferably by a Maillard-type of reaction. Browning can be obtained by Maillard

WO 94/00996

reactions (amino sugar reactions), by caramelization of sugars or by oxidative reactions. Examples of Maillard compositions are lactose, preferably in combination with a protein-source, such as milk products containing lactose.

5

The stability of the water-continuous emulsion is greatly dependent on the droplet size of the fat droplets in the emulsion. Droplet sizes of less than 5.0 μ m, in particular of 0.5-2.0 μ m, are preferred.

10

15

20

25

30

35

We also found that the presence of some egg-yolk in our composition leads to an improved emulsion stability. Therefore, we prefer that our ready-to-use glazing agents also comprise 1-10 wt% in particular 2-8 wt% of an egg-yolk composition. Preferred egg yolk compositions contain some salt, in particular 5-15 wt% (on egg yolk).

The glazing agents according to the invention can be applied on normal dough (i.e. of ambient temperature) and on frozen dough. Baking of the dough, with or without thawing of the dough before baking, leads to excellent gloss, appearance and colour of the baked products.

The glazing agent is normally applied in amounts of 30-100 mg/cm². Spraying or atomizing are standard techniques for the distribution of the glazing agent; however, brushing should also be possible.

Although above products display excellent glazing properties, we found that upon use (by spraying) of the glazing agent over the product to be baked, which normally is performed on a baking-sheet, the part of the material, that is in direct contact with the hot baking-sheet is very difficult to remove from the baking sheet after baking of the product.

In order to improve the cleaning abilities of our glazing

agents, we found that addition of 0.05-2.5 wt% of a pyrophosphate, in particular 0.1-1.5 wt%, resulted in the required improvement. Preferred pyrophosphates are the alkali-pyrophosphates, preferably sodium pyrophosphate.

5

Good results have been obtained by any of the following procedures:

- I 1. making a dough, moulding and proofing it;
- 2. coating it with glazing agent;
 - 3. baking of fresh product.
 - II 1. making a dough and moulding it;
 - coating it with glazing agent;
- 3. baking of fresh product.
 - III 1. making a dough, moulding and proofing it;
 - coating it with glazing agent;
 - 3. freezing of the coated product;
- 4. frozen storage : 3 weeks;
 - 5. baking of the frozen product without thawing.
 - IV 1. making a dough and moulding it;
 - 2. coating of the dough with glazing agent;
- 3. freezing of the coated dough;
 - 4. frozen storage : different periods;
 - 5. thawing of the frozen, coated dough;
 - 6. proofing of the product of 5);
 - 7. baking of the product of 6).

30

- V 1. making a dough and moulding it;
 - coating it with glazing agent;
 - freezing of the dough;
 - 4. frozen storage : different periods;
- 35 5. thawing;
 - 6. baking of the coated, thawed, frozen dough.

In process IV, relative humidity has an impact on the product properties. It was found that too high an R.H. (i.e. > 60%) led to relatively worse products.

It is also possible to apply the glazing agent according to the invention for the preparation of microwavable, proofed, baked, frozen and coated doughs.

EXAMPLES

10

I A pre-mix was made in water of 80°C containing the water, skimmed milk powder and sodium caseinate.

Simultaneously, a mixture of unsaturated mono- and diglycerides was dissolved in soybean oil ($N_{20} \approx 0$).

The fat mixture was added to the water phase and the mixture was subjected to Ultra Turrax mixing for 5 minutes. The D_{3.2} (= droplet size) was 3.8 μ m.

20

The composition was sterilized by indirect heat treatment (8 seconds at 140°C).

The composition of the resulting glazing agent was :

25

	•	wt.%
	Water	80.0
	Na-caseinate	10.0
	SMP	2.0
30	во	7.9
	Emulsifier	0.06

The viscosity (η_{20}) of the sterilized product was about 200 mPa.s.

35

II The procedure of Example I was repeated; however, the Ultra Turrax mixing was followed by a pressure-

homogenization procedure (at about 50 bar). This resulted in a product having a droplet size before sterilization of about 1.9 μm . The η_{20} of the sterilized product was about 100 mPa.s.

5

III The products were evaluated on the following product types: Dänische Brötchen, croissants, puff pastry sheets and "gevulde koeken" (≈ almond paste cakes).

Therefore, the procedures mentioned above (I-V) were applied, as illustrated in Table I.

TABLE 1	Products	Yeast-leavened Laminated dough: Short dough: laminated dough: Puff pastry 'gevulde koeken' croissants sheets (≈ almond paste cakes)	Sample number	2	3 4	· ·		8/2	8	9 10
		Yeast-leavened Yerich dough:		1				w v	o	
	Procedure			Ι	II	III Frozen storage: 3 weeks	IV Frozen storage:	2 weeks 3 weeks	908 - KH 458 - RH	V 2 weeks

WO 94/00996 PCT/EP93/01704

5

In Tables II and III a comparison is made between coatings obtained with the composition according to the invention, coatings obtained from whole egg and coatings obtained with a commercially available, not ready-to-use mix "Ovex bakglans" (ex Zeelandia).

1			

'Dänische Brötchen'	Whole egg reference	OVEX bakglans	1	Sampl 2 3	e n u m	ber 5	7	8
Gloss remarks:	3	2	3					
Appearance remarks:	3	2	3					
Colour remarks:	3	8	က					
Mouthfeel crust remarks:	3	ε	3.5					
Croissants	Whole egg reference	OVEX bakglans	1	Sampl 2 3	e num	m ber S	7	8
Gloss remarks:	3			4		4	3	4
Appearance remarks:	3			4		4	3	4
Colour remarks:	3			e,		က	3	r
Mouthfeel crust remarks:	3							

വ

20

			TABLE II (c	(cont.)				
Puff pastry Sheets	Whole egg reference	OVEX bakglans	1 2	S a m p l	e numb	9 Q	7	80
Gloss remarks:	3	m		3				
Appearance remarks:	က	3		က				
Colour remarks:	3	3		3				
Mouthfeel remarks:	3	3.5		3.5				
'Gevulde Koeken' (≈ almond paste cakes)	Whole egg reference	OVEX bakglans	L1	S a m p 1	e n u m b 4	а 5 5 1 1 1 1 1	7	8
Gloss remarks:	3	3			က			
Appearance remarks:	3	4			4			
Colour remarks:	ю	, 4			4			
Mouthfeel remarks:	3	3			3			

10

Ŋ

	SCALE			
	Gloss	1	3	5
		less	reference	more
5			(whole egg)	
	Colour	1	3	5
	0020	less	reference	more
			(whole egg)	
LO			_	_
	Appearance	1	3	5
		worse	reference	better
	t	han ref.	(whole egg)	than ref.
15	Mouthfeel cr	ust 1	3	5
		less	reference	tougher
		tough	(whole eag)	

TABLE III

Glazing OVEX bakglans Type of glazing according to agent the invention Sample number 2 weeks' storage poor results: poor results: 6 very dark surface very dark surface which which showed showed strange strange bubbles bubbles smooth surface smooth surface: 9 yellow-brown light-yellow colouring; good colouring; good appearance appearance smooth surface smooth surface 10 light-brown light-yellow colouring; good colouring; good appearance appearance

10

5

EXAMPLE IV

A pre-mix was made in water of 80°C containing the water, skimmed milk powder and sodium caseinate.

Simultaneously, a mixture of Na-pyrophosphate, unsaturated mono- and diglycerides was dissolved in soybean oil ($N_{20} \approx 0$).

The fat mixture was added to the water phase and the mixture was subjected to Ultra Turrax mixing for 5 minutes. The D $_{3.2}$ (= droplet size) was 3.8 μm .

25

The composition was sterilized by indirect heat treatment (8 seconds at 140°C).

The composition of the resulting glazing agent was:

		wt%
	Water	80.5
	Na-caseinate	9.0
	SMP	2.0
5	во	7.94
	Emulsifier	0.06
	Na-pyrophosphate	0.5

The viscosity (n_{20}) of the sterilized product was about 200 mPa.s.

An aluminium baking sheet was provided with a thin fatlayer. On this fatlayer a layer of the glazing composition was brought, using a pensil. The system so obtained was heated for 15 min. in an oven at 190°C.

Above procedure was repeated using 1) a whole egg glazing composition and 2) a glazing agent as above, but without Na-pyrophosphate.

The baking sheets were cooled for 30 min. after removal from the oven. Cleaning was performed by soaking for 3 min. with water of 55°C.

25 Results:

15

20

TABLE IV

	agent	cleaning results
0	whole egg	++
	glazing agent without pyrophosphate	
	glazing agent with pyrophosphate	++

CLAIMS

1. Ready-to-use glazing agent comprising a fat-in-water emulsion with the composition :

1-25 wt.% of a liquid vegetable oil; 5-15 wt.% of casein or its salts;

0.005-10 wt.% of an emulsifier, in particular one selected from the group of fatty acid monoglycerides and diglycerides from $\rm C_{14}\text{-}C_{22}$ fatty acids;

0.1-8.0 wt.% of a composition giving a browning upon heating, preferably by a Maillard-type reaction, such as lactose, or a milk product containing lactose;

balance : water.

- 2. Ready-to-use glazing agent according to Claim 1, wherein 5-15 wt.% of liquid vegetable oil is present.
- 3. Ready-to-use glazing agent according to claims 1 or 2, wherein the liquid vegetable oil also comprises 2-15 wt% (on oil) of a hydrogenated vegetable fat, in particular hydrogenated palm oil.
- 4. Ready-to-use glazing agent according to Claim 1, wherein 8-11 wt.% of casein or its salts are present.
- 5. Ready-to-use glazing agent according to Claim 1, wherein 0.01-1.0 wt.% of emulsifier is present.
- 6. Ready-to-use glazing agent according to Claim 1, wherein the emulsifier is a mixture of monoglycerides and diglycerides from $\rm C_{16}-\rm C_{18}$ saturated and/or unsaturated fatty acids.
- 7. Ready-to-use glazing agent according to Claim 1, wherein 0.3-3 wt.% of lactose or a milk product containing lactose is present.

- 8. Ready-to-use glazing agent according to Claim 1, wherein the viscosity of the composition at 20°C is 1-10⁵ mPa.s.
- 9. Ready-to-use glazing agent according to any of Claims 1-8, wherein the glazing agent is sterilized.
- 10. Ready-to-use glazing agent according to Claim 9, wherein the glazing agent has an ambient shelf-life of more than 3 months.
- 11. Ready-to-use glazing agent according to Claim 1 or 2, wherein the liquid vegetable oil has a solid fat index at 20°C of at most 7.0.
- 12. Ready-to-use glazing agent according to Claim 1 or 7, wherein the milk product is skimmed milk powder or buttermilk powder.
- 13. Ready-to-use glazing agent according to any of Claims 1-12, wherein the droplet size of the emulsion is less than 5.0 μm .
- 14. Ready-to-use glazing agent according to any of claims 1-13, wherein the glazing agent comprises additionally 0.05-2.5 wt% of a pyrophosphate, in particular 0.1-1.5 wt% of a pyrophosphate of an alkaline metal.
- 15. Ready-to-use glazing agent according to claims 1-14, wherein the glazing agent also comprises 1-10 wt%, in particular 2-8 wt% of egg-yolk.
- 16. Deep-frozen, non-baked food products on which a coating layer of a glazing agent is present, wherein the glazing agent has the composition according to any of Claims 1-15.

- 17. Baked products, including deep-frozen baked, non-frozen baked and gas-packed baked or parbaked food products provided with a coating layer of a glazing agent, wherein the coating is obtained from a composition according to any of Claims 1-15.
- 18. Use of a glazing agent as a coating layer for baked food products, wherein the glazing agent according to any of Claims 1-15 is applied for the improvement of the gloss, appearance and/or colour of baked, deep-frozen, laminated food products.

International Application No

L CLASSIF	TCATION OF SUBJE	CT MATTER (if several classification sy	mbois apply, indicate all)6	
		Classification (IPC) or to both National Cl		
	5 A21D13/0			
			•	
II. FIELDS	SEARCHED			
	·	Minimum Docume	ntation Searched?	
Classificati	on System		Classification Symbols	
				
Int.Cl.	. 5	A21D; A23G		
		Documentation Searched other t		
		to the Extent that such Documents a	re included in the Fields Dearched	
				ļ
- 200W	CONTROL CONTROL	D TO BE RELEVANT		
Category °		ocument, 11 with indication, where appropria	to of the missour extraor 12	Relevant to Claim No.13
Category	Chance of Di	Remark - with indication, where appropria	ne, or me records persons	ROCFALL TO CHAIR TO
Υ	EP.A.O	205 195 (UNILEVER PLC)		1-15
	17 Decei	mber 1986		
		n the application		
	see the	whole document		
Υ	US,A,4	389 420 (S.H. YONG ET A	L.)	1-15
	21 June	1983	•	
	see cla	ims		
A	DE.A.2	303 703 (C.H. BOEHRINGE	R SOHN)	
	1 Augus		•	
	AUL A C	B13 493 (ABBOTT LABORAT	ODIES)	
^	24 Marc	13 433 (ABBUTT LABUKAT) h 1970	ories)	
A		596 826 (S.J. LEUSNER E	T AL.)	1-3,14
		ember 1987 whole document		•
	see one	#11010 Gocalicito		
			-/	
Special	categories of cited do	cum ente - 10	"T" later document published after the interna	tional filing date
"A" doc	nument defining the ge	neral state of the art which is not	or priority date and not in conflict with the	e application but
	isidered to be of partic lier document but publ	ular relevance ished on or after the international	invention "X" document of particular relevance; the clai	• •
អូរ	ng date	w doubts on priority claim(s) or	cannot be considered novel or cannot be dipolive an inventive step	
whi		the publication date of another	"Y" document of particular relevance; the clai	
"O" doc	cument referring to an	oral disclosure, use, exhibition or	cannot be considered to involve an invent document is combined with one or more of ments, such combination being obvious to	ther such docu-
"P" doc		to the international filing date but	in the art.	
late	er than the priority dat	e daimed	"&" document member of the same patent fan	illy
IV. CERTI	FICATION			
Date of the	Actual Completion of	the International Search	Date of Mailing of this International Sear	ch Report
	18 OCTO	BER 1993	2 2. 10. 93	
Internationa	I Searching Authority		Signature of Authorized Officer	
		AN PATENT OFFICE	BEVAN S.R.	
	.,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,			

INTERNATIONAL SEARCH REPORT

	INTERNATIONAL SEARCH REPORT	
	International Application No	PCT/EP 93/01704
III. DOCUM	ENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)	
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	DATABASE WPI Section Ch, Week 7117, Derwent Publications Ltd., London, GB; Class D12, AN 71-28631S & JP,B,46 015 658 (NIPPON CHEMICAL IND. CO. LT.) see abstract	1,14
A	FR,A,2 268 476 (HENKEL & CIE G.M.B.H.) 21 November 1975 see claims	1,14
	·	
		-
	10 textra short) Liserary (QIS)	

Form PCT/ISA/210 (extra sheet) (Jamesty 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

ΕP 9301704 SA 76563

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

18/1 18/10/93

Patent document cited in search report	Publication date		nt family mber(s)	Publication date
EP-A-0205195	17-12-86	NL-A- AU-B- AU-A- DE-A- US-A-	8501283 567235 5715186 3660523 4762721	01-12-86 12-11-87 13-11-86 22-09-88 09-08-88
US-A-4389420	21-06-83	None		*************
DE-A-2303703	01-08-74	GB-A- JP-C- JP-A- JP-B-	1443892 1114003 49108256 56049528	28-07-76 16-09-82 15-10-74 24-11-81
NL-A-6813493	24-03-70	None		
US-A-4696826	29-09-87	CA-A-	1316751	27-04-93
FR-A-2268476	21-11-75	DE-A- BE-A- NL-A- SE-A-	2420622 828378 7503914 7503778	13-11-75 27-10-75 29-10-75 28-10-75